



Electrochemical reduction of carbondioxide on polypyrrole coated copper electro-catalyst under ambient and high pressure in methanol



Rezzan Aydın^{a,*}, Hülya Öztürk Doğan^b, Fatih Köleli^a

^a Department of Chemistry, Faculty of Arts and Sciences, Mersin University, Mersin 33342, Turkey

^b Department of Chemistry, Faculty of Arts and Sciences, Ataturk University, Erzurum 25240, Turkey

ARTICLE INFO

Article history:

Received 14 December 2012

Received in revised form 25 March 2013

Accepted 9 April 2013

Available online 30 April 2013

Keywords:

CO₂ reduction

Copper

Polypyrrole electrode

High pressure

Methane

ABSTRACT

The electro-reduction of CO₂ was investigated on a polypyrrole-coated copper catalyst, for the first time. The experiments were carried out at different pressure conditions (1, 10, 20, 40 and 60 bars), varying film thicknesses (0.5, 0.9, 1.4, 2.1 and 5.4 μm) and at different potential values (−0.8, −1.0, −1.5, −2.0, −2.5, −3.0 V Pb(Hg)_x/PbSO₄/SO₄^{2−}) in CH₃OH/0.1 M LiClO₄/H⁺ electrolyte system. At −0.8 V and −1.0 V, it was obtained only HCOOH and CH₃COOH. At more negative values, gaseous products such as CH₄, C₂H₄, C₂H₆ and CO were detected, additionally. The coating of copper electro-catalyst with a conducting polymer causes a shifting of the product distribution to hydrocarbons, especially to methane.

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1. Introduction

Carbondioxide is considered to possess a serious effect on global warming. The fixation of the waste carbondioxide is one of the most interesting research topics of contemporary scientific world. Many studies were carried out for fixing this waste carbon source to useful compounds [1–18]. Carbondioxide can be converted by various techniques; radiochemically, chemically, thermochemically, photochemically, biochemically and electrochemically [1,2]. Among them, the electrochemical conversion seems to be the most powerful technique to reduce CO₂ into valuable chemicals.

Employing of bulk metals as electro-catalyst leads to different products published in the literature [3,5–8,10,12,13,16–19]. In aqueous solution, the main product is formic acid on *sp*-group metals, such as Hg, In, Sn and Pb [20]. On metals of *d*-groups, i.e. Pt, Ni and Co however, CO is favored in aqueous solution. In nonaqueous solution, catalysts lead to different product distribution. For example, oxalic acid was obtained selectively on Tl, Pb and Hg [20]. Carbonmonoxide can be produced mainly on Fe, Cr, Mo, Pt [2,6–8,16,20–35]. Among all metals, copper has a special place because its catalytic activity tends to produce more hydrocarbons such as CH₄, C₂H₄, C₂H₆ in protic as well as in aprotic milieu [19–26].

Generally, we can say that bulk metal electrodes need disadvantageously high negative overpotentials for CO₂ conversion. For

example, an extreme value of −7 V was needed for reduction of CO₂ in a nonaqueous media on a blank copper to produce hydrocarbons [19–26]. To decrease this high value, also Cu alloys were employed such as Cu–Ni, Cu–Sn, Cu–Pb, Cu–Zn, Cu–Cd and Cu–Ag [25–29]. However, regarding high overpotential values even the usage of these alloys was not benefitable enough but Faradaic efficiencies became more efficient compared to blank Cu [6–8].

Recently, we studied the role of conducting polymers deposited on Pt electrodes onto CO₂ reduction and found that coating of a metal surface with conducting polymers causes a dropping of the overpotential drastically up to ca. −0.4 V (Ag/AgCl) for formic acid formation [3,4,10–15]. In accordance with our previous studies, now, we employed polypyrrole deposited Cu for the electro-reduction of CO₂ with the aim to obtain direct combustibles methane and formic acid, at lower overpotential values.

2. Experimental

A standard H-type cell (Aldrich Nafion® 117) was used for cyclic voltammetric (CV) studies. A copper wire (% 99.9) having 3.8×10^{-2} cm² surface area was used as a working electrode. A platinum plate (1 cm²) as counter electrode and an Ag/AgCl (saturated KCl) reference system were employed for the voltammetric studies. The copper wire was embedded in an acrylic cylinder and the bottom was polished with 1500 grid emery paper to clean the surface from oxides and other contaminations. The prepared surface was washed with distilled water and dried.

A divided (Aldrich Nafion® 117), high-pressure cell introduced before [3,4,13–15,30,31], was used for preparative electrochemical

* Corresponding author. Tel.: +90 537 5136738; fax: +90 324 3610046.

E-mail address: rezzanaydin@gmail.com (R. Aydın).

reduction of CO_2 in a pressure range from 1 bar to 60 bar. Throughout the preparative experiments, the working electrode was a copper plate (8 cm^2). Same electrode was coated electrochemically with polypyrrole (PPy) film at 0.9 V [Ag/AgCl] in a 0.2 M sodium oxalate (NaOx) solution containing 0.5 M of pyrrole [32,33]. The film thicknesses (0.5, 0.9, 1.4, 2.1 and $5.4 \mu\text{m}$) were calculated through passed charge by using the equation of Holdcraft and Funt, successively [34]. The passed charge was measured with a coulombmeter (Denko, HF-201) in dependence on time for each thickness. Subsequently, with freshly prepared electrode, we carried out a new experiment and determined the optimum film thickness according to the Faradaic efficiencies, experimentally. Polymer film morphology was displayed by SEM micrographs (Zeiss, Supra 55).

For all experiments, the electrolyte was $\text{CH}_3\text{OH} + 0.1 \text{ M LiClO}_4$ and as proton source was added $1.5 \times 10^{-3} \text{ M H}_2\text{SO}_4$ into the electrolyte solution.

During the experiments under ambient pressure, CO_2 was bubbled for 30 minutes at a rate of $40 \text{ cm}^3 \text{ min}^{-1}$. High-pressure experiments were done at 10, 20, 40, and 60 bars in a CO_2 atmosphere. In the absence of CO_2 in the solution, no product was detected on blank Cu and on PPy coated by electrolysis under ambient and under high pressure.

To keep the potential constant under high-pressure conditions, we used a reference electrode $\text{Pb}(\text{Hg})_x/\text{PbSO}_4/\text{SO}_4^{-2}$ (home made; a reference potential of +250 mV ([Ag/AgCl]) [30,31] and the counter electrode was a platinum plate (7 cm^2). This constitution of the cell-system allows us to study the reactions under high pressure as well as other extreme conditions electrochemically. All presumable products of CO_2 reduction on copper is well known and commercial purchasable. These substances were bought and used as reference substances for chemical analyses. Detected gaseous and liquid substances were compared gas-chromatographically with these reference substances on the GC (Hewlett–Packard, HP6890) by using a QS-propack column. The Faradaic efficiencies for products were calculated with measured (passed) charges.

3. Results and discussion

In the following sections, we are going to discuss starting with analytical investigation, than preparative electrolysis and the influence of the changed parameters (applied potential, film thickness, and pressure) on the product formation. Finally, a reaction mechanism was proposed.

3.1. Voltammetric investigations

In the absence of CO_2 , the cyclic voltammogram (CV) of Cu shows a small wave at -0.75 V which belongs to Cu and it is specific for this metal [32,33]. This small wave disappears with coating of the surface with polymer film. Otherwise, in CV of Cu, there is no waves up to ca. -1.3 V where hydrogen evolution starts (Fig. 1-I).

In the presence of CO_2 , the wave to $\text{H}_{(\text{ad})}$ formation at ca. -0.7 V is only slightly visible in the CV of blank Cu and up ca. -1.2 V (pH 3.2) hydrogen evolution starts apparently (Fig. 1-II).

In the absence of CO_2 , in contrast to blank Cu, the wave at ca. -0.7 V have slightly more currents on coated Cu. In the negative direction, the electrode is passivated through the polymer film and shows no activity (Fig. 1-III).

In the presence of CO_2 , on the PPy coated electrode, the $\text{H}_{(\text{ad})}$ formation was intensified and the wave on the curve become noticeable (Fig. 1-IV). In other words, the formation of $\text{H}_{(\text{ad})}$'s occurs with polypyrrole coating at more positive potentials and this, the decreasing of overpotential for $\text{H}_{(\text{ad})}$ formation, appears to be the ultimate role of the thin film on the metal surface. We suggest that through the deposition of polymer a film, $\text{H}_{(\text{ad})}$ formation in and on

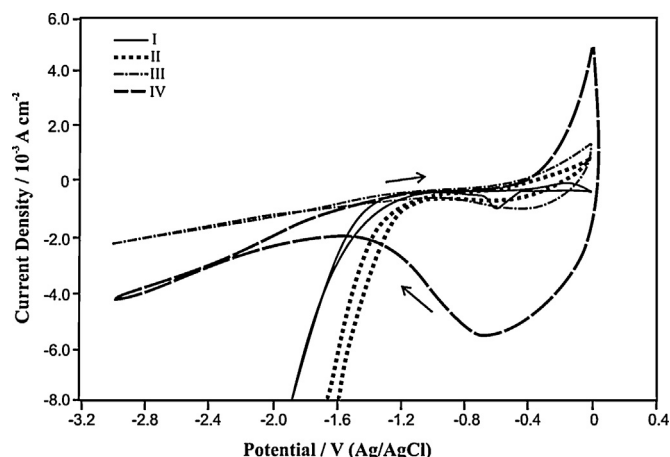


Fig. 1. Electrochemical behaviour of copper electrode; coated and uncoated PPy in $\text{CH}_3\text{OH}/0.1 \text{ M LiClO}_4/1.5 \times 10^{-3} \text{ M H}^+$ electrolyte. I – blank copper without CO_2 , II – blank copper with CO_2 , III – Cu-PPy without CO_2 , IV – Cu-PPy with CO_2 . $\nu = 20 \text{ mV s}^{-1}$.

the film is supported while the hydrogen evolution (recombination of $\text{H}_{(\text{ad})}$ atoms) on the metal surface are suppressed in a wide potential range. The suppression of a sharp hydrogen evolution extends the potential window up to -3.0 V and we could carry out preparative electrolysis until this value (to make our result comparable with the literature, too).

The solubility of CO_2 in methanol is 5 times higher than in aqueous electrolytes why we used $\text{CH}_3\text{OH}/0.1 \text{ M LiClO}_4$ as electrolytic solution. However, almost any product of CO_2 reduction needs hydrogen ($\text{H}_{(\text{ad})}$ atom) as a reactant, hence a well defined amount of protons were added in form of $1.5 \times 10^{-3} \text{ M H}_2\text{SO}_4$ in the solution.

The cyclic voltammograms of PPy coated Cu without and with acid addition are presented in Fig. 2.

Polypyrrole coated copper shows no activity in the absence of acid in the CO_2 saturated solution (Fig. 2-I). After addition of acid in the same solution, a wide reduction wave at ca. -0.7 V is getting visible due to the formation of $\text{H}_{(\text{ad})}$ atoms (Fig. 2-II).

3.2. Preparative electrolysis

The fixation of CO_2 on blank copper is described in the literature [19–25]. Most of these works are carried out at extremely negative overpotentials by using alkali-hydroxides in solutions. In aqueous medium, products were CH_4 , C_2H_4 , C_2H_6 , CO , HCOOH , $\text{C}_2\text{H}_5\text{OH}$,

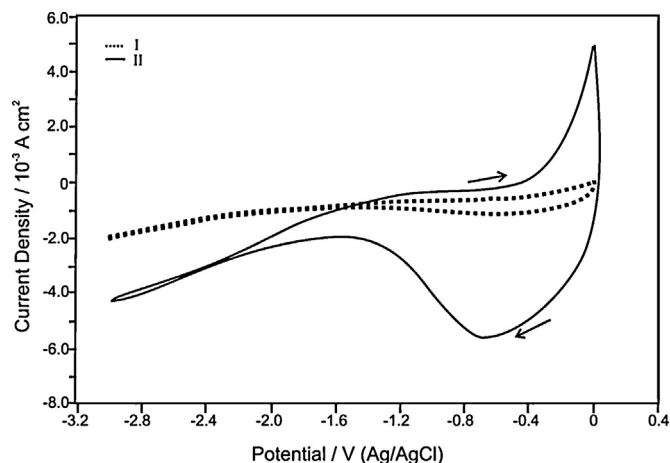


Fig. 2. Electrochemical behaviour of PPy deposited Cu electrocatalyst (film thickness: $1.4 \mu\text{m}$) in $\text{CH}_3\text{OH}/0.1 \text{ M LiClO}_4$ electrolyte; I – without acid addition; II – with addition of $1.5 \times 10^{-3} \text{ M H}_2\text{SO}_4$. $\nu = 20 \text{ mV s}^{-1}$.

Table 1

Faradaic efficiencies of CO₂ reduction products versus applied potential on a PPy coated Cu electrocatalyst in CH₃OH/0.1 M LiClO₄/1.5 × 10^{−3} M H⁺. Pressure: 20 bar; electrolysis time: 3 h; film thickness: 1.4 μm.

Potential (V)	Faradaic efficiency (%)				
	CH ₄	C ₂ H ₄	CO	HCOOH	CH ₃ COOH
−1.0	NA ^a	NA	NA	22	47
−1.5	25.1	2.1	22	15	27.5
−2.0	24.8	1.8	24	16	28
−2.5	25.1	1.8	22	20.1	30.1
−3.0	25.5	3.1	15.1	19.8	40.2

^a NA: not analysed.

C₃H₇OH and in nonaqueous medium CH₄, C₂H₄, CO, HCOOH commonly [20,35]. In contrast to these existing studies, we carried out our experiments in acidic methanol and under pressure (20 bars) on a PPy coated Cu starting at a more positive potential of −0.8 V. Even at −0.8 V, we obtain a Faradaic efficiency of ca. 22% for formic acid formation (no hydrocarbons). Ultimately, acetic acid was detected as byproduct. The formation of acetic acid is inevitable (see mechanism) in acidic methanol solution, although it is a valuable product too. Until −1.5 V we could not detect any gaseous products by carefully analysis. Recently, at −1.5 V the gaseous products could be detected with valuable Faradaic efficiencies (Table 1).

It has been reported that CO is the main product on blank copper in alkaline solution [19,35–38]. In the case of PPy coated Cu, however, the CO formation is suppressed in acidic medium and we have CH₄ as main gaseous product. Acetic acid was detected throughout the scale of applied potential. Ethane was found only in trace. As mentioned above, valuable Faradaic efficiencies for CH₄ and HCOOH were obtained at −1.5 V. However, to compare our results with that of the literature, we applied potentials up to relatively high negative values. But, the experiments showed that the Faradaic efficiencies were not changed seriously also until −3.0 V. For example the aimed compound, CH₄ was produced just at −1.5 V with ca. 25% of a Faradaic efficiency (highest value in the literature) and this remained almost constant until −3.0 V. For C₂H₄ and especially for C₂H₆, Faradaic efficiencies remain very low. Results, achieved in this study and published in literature are presented to comparison in Table 2.

The employing of a PPy deposited Cu turns the product spectrum visibly to hydrocarbons. To clarify these effect, product distributions on both blank Cu and PPy coated Cu, are presented in Fig. 3.

By employing of PPy-Cu, the product distribution was changed to the aimed product methane regarding the Faradaic efficiencies from 5% to 25%, while the production of acetic acid suppressed remarkable from ca. 70% to 40%. Another rise of Faradaic efficiency was achieved at HCOOH and CO by changing of the catalyst (Fig. 3). This behaviour can be explained with the change of production rate in the H_(ad) formation, hence the recombination of H_(ad) atoms

Table 2

Comparison of Faradaic efficiencies of the CO₂ reduction products between literature and present work in methanol.

Lit.	Electrode–Electrolyte	p (atm)	V (Volt)	CH ₄	Faradaic efficiency (%)				
					C ₂ H ₄	CO	HCOOH	H ₂	CH ₃ COOH
1 [35]	Cu–CH ₃ OH/LiCl	10	−3	20	1.5	60	10	10	–
2 [36]	Cu–CH ₃ OH/CsOH	10	−3	0.9	5	70	10	2	–
3 [37]	Cu–CH ₃ OH/KOH	A ^b	−3	10.8	27.9	13.9	8.5	2.6	–
5 [38]	Cu–CH ₃ OH/BAC ^a	A ^b	−2.2	18.9	16.9	31.8	–	1.3	–
6 [19]	Cu–CH ₃ OH/CsOH	A ^b	−3	6	1	27	13	22	–
7 ^d	Cu–PPy–CH ₃ OH/LiClO ₄ /H ⁺	20	−3	25.5	2.9	14.9	19.1	NA ^c	40.2

^a Benzalkonium chloride.

^b A: ambient pressure.

^c NA: not analysed.

^d Present work.

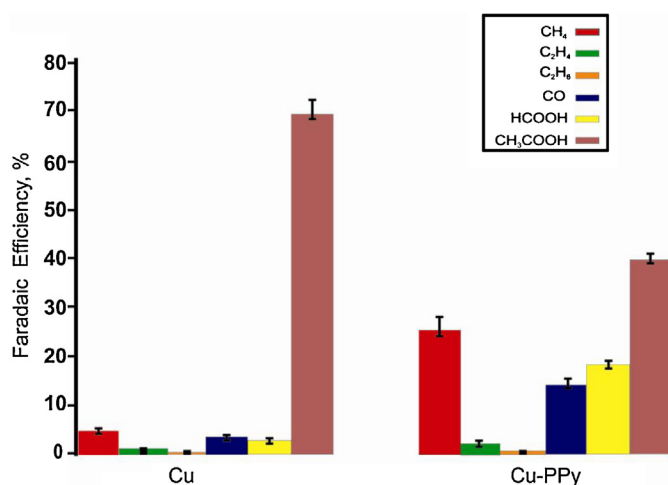


Fig. 3. Faradaic efficiencies to formed products of CO₂ reduction on blank Cu and Cu-PPy electrocatalysts in CH₃OH/0.1 M LiClO₄/1.5 × 10^{−3} M H⁺. Pressure 20 bar; electrolysis time 3 h; film thickness 1.4 μm.

Table 3

Faradaic efficiencies of CO₂ reduction products with film thickness on a PPy coated Cu electrocatalyst in CH₃OH/0.1 M LiClO₄/1.5 × 10^{−3} M H⁺. Potential: 3.0 V; pressure: 20 bars; electrolysis time: 3 h.

Film thickness (μm)	Faradaic efficiency (%)				
	CH ₄	C ₂ H ₄	CO	HCOOH	CH ₃ COOH
0.5	21.1	2.2	10.2	24.2	36.3
0.9	23.2	2.3	12.9	21.1	38.2
1.4	25.5	3.1	15.1	19.8	40.2
2.1	25.2	3.1	18.2	18.2	34.1
5.4	25.1	3.1	20.2	18.7	20.1

hindered through the polymer film and as the result, hydrogen evolution was impeded.

3.3. Film thickness

According to our previous experiences, the film thickness is an important parameter during the preparation of an electro-catalyst with conducting polymers [3,4,13–15,30,31]. In case of a too thick film, the metal surface covered fully up and the catalyst is passivated or the film is too thin, the electrode under the film keeps his metallic character and the coverage is not efficient enough for the reaction.

In case of PPy coated Cu, to achieve the highest Faradaic efficiencies, we prepared the same Cu plate with different film thicknesses of 0.5, 0.9, 1.4, 2.1 and 5.4 μm, successively and carried out a new experiment with each of the prepared electrodes (Table 3). Preparative electrolysis provided the best results by a film thickness of

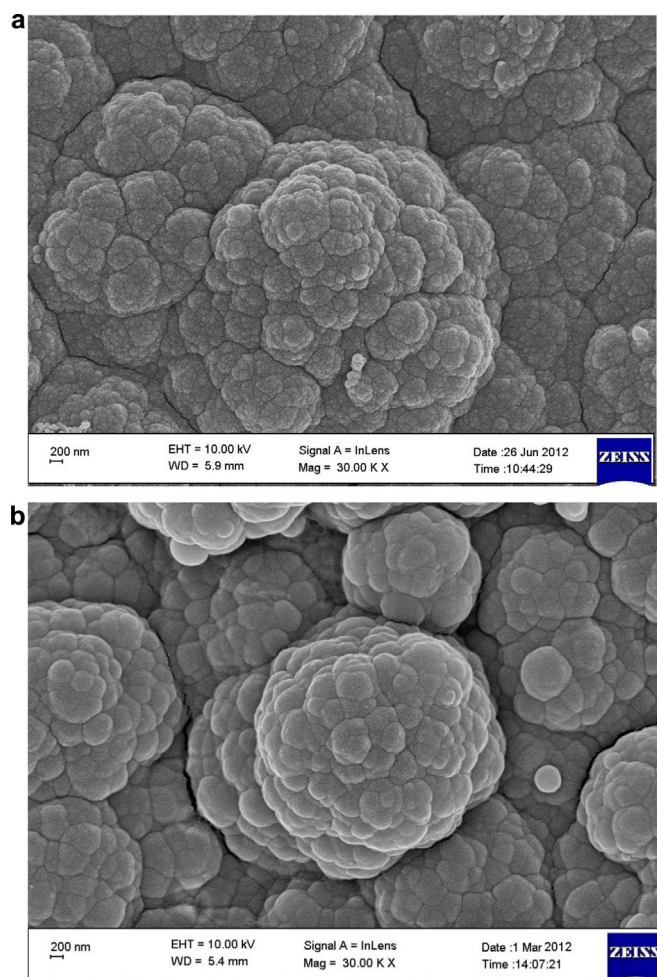


Fig. 4. SEM micrographs of a Cu-PPy electrode; (a) before electrolysis, (b) after electrolysis.

1.4 μm . Polymer film is stable and as can be seen in SEM micrographs, before and after electrolysis there is no changes or damages visible in the cauliflower structure of polymer film (Fig. 4a and b).

3.4. Influence of pressure

To study the influence of applied pressure on the product formation, experiments were carried out at ambient pressure and at 10, 20, 40 and at 60 bars, successively. As can be seen in Table 4, 20 bars were found to be as the optimum pressure value regarding the highest Faradaic efficiencies of targeted products. Methane was formed with increasing Faradaic efficiency until 20 bars continuously. With further increasing of pressure, the Faradaic efficiencies for methane formation begins to decrease while for

Table 4

Faradaic efficiencies of formed products of CO_2 reduction versus applied pressure on a PPy coated Cu electrocatalyst in $\text{CH}_3\text{OH}/0.1 \text{ M LiClO}_4/1.5 \times 10^{-3} \text{ M H}^+$. Potential: 3.0 V; film thickness: 1.4 μm ; electrolysis time: 3 h.

$p(\text{CO}_2)$ (bar)	Faradaic efficiency (%)				
	CH_4	C_2H_4	CO	HCOOH	CH_3COOH
1	3.2	0.5	22.2	6.2	50.2
10	16.4	4.1	17.8	15.2	48.4
20	25.5	3.1	15.1	22.1	40.2
40	13.1	3.0	14.2	24.1	39.1
60	6.3	2.2	13.1	25.4	40.1

formic acid formation arises up to ca. 22% and further increase of pressure causes no remarkable changes in the product distribution.

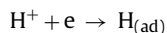
3.5. Mechanism

Formulations to the mechanism of CO_2 reduction were classified according to two different medium, namely protic and aprotic. In case of protic medium on metal electro-catalysts, the establishing of format ions is preferred and the main organic product is HCOOH . Contrarily, in aprotic medium the product distribution depends primarily on the employed electrode material and by using of copper especially, hydrocarbons, such as CH_4 , C_2H_4 , C_2H_6 [2,16,21,23,24,33–44] and format ions were provided.

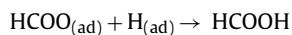
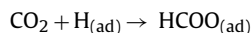
Although, methanol itself can be considered as a protic solvent, the concentration of the protons, due to self-ionization, is rather low and the formation of hydrocarbons remains very limited. The addition of a well-defined amount of protons in the solution provide an increased formation rate of $\text{H}_{(\text{ad})}$ atoms. It is noticeable that there is a sensitive equilibrium in respect to the concentration of added protons into the solution. If the concentration is too high, the reaction tends to hydrogen evolution. In case of a too low proton concentration, the reaction rate drops (too low currents) and the electrolysis time arises. Through detailed investigations, the optimum concentration of added protons was found to be as $1.5 \times 10^{-3} \text{ M}$.

The dependence of product formation on the proton concentration in the solution leads us to the conclusion that the reaction mechanism is a hydrogenation and not a direct electron transfer to the currently employed CO_2 molecule. This assumption corresponds with our previously results so that the fixation of CO_2 as well as of N_2 [30,31] obeys a hydrogenation mechanism if a conducting polymer coated metal is used.

In case of copper, it has with -0.8 V [NHE] a definitive higher overpotential for hydrogen evolution than platinum (-0.3 V) [45] that is why our preparative experiments were started at this potential and closed to -3.0 V . As mentioned above, a direct electron transfer at this low overvoltage is thermodynamically not possible and in the case of a hydrogenation, the first step must be the adsorption of a proton and formation of a $\text{H}_{(\text{ad})}$

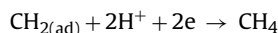
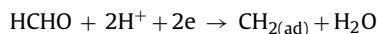
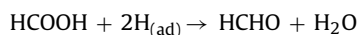


Subsequently the transfer of formed $\text{H}_{(\text{ad})}$ to a CO_2 molecule

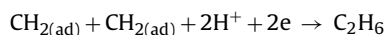
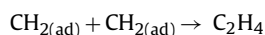


leads to formic acid. This reaction was investigated in detail and reported closely in the literature [3,4,9–15].

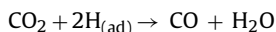
The formation of the gaseous products needs definitive more $\text{H}_{(\text{ad})}$ atoms for forming of CH_4 and/or other hydrocarbons. The first possible idea appears, for CH_4 formation, an executive hydrogenation all intermediates [3,4]



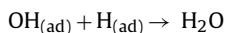
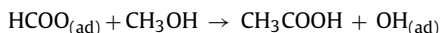
and for further compounds



can be formulated.



For CH_3COOH we suggest [3,4]



4. Conclusion

Conclusively, we studied the fixation of CO_2 on a polypyrrole modified Cu for the first time with the ultimate goal to obtain usable fuel substances such as CH_4 and HCOOH . The coating of the Cu surface with polypyrrole leads to a controlled hydrogen evolution and compared to the blank Cu as electro-catalyst, formation of hydrocarbons begins at lower overpotentials with high Faradaic efficiencies. In this sense, a successfully conversion of waste CO_2 in technical scale could be a benefitable process from the point of environmental view whereby optimum reaction conditions were determined with variation of some significant parameters such as potential, pressure, film thickness and concentration of proton donors in the electrolytic medium. With the establishing optimum values of mentioned parameters, the highest Faradaic efficiencies (ca. 25% for CH_4 and 20% for HCOOH) were obtained, as known until now.

Acknowledgement

We wish to express our thanks to the Mersin University Research Foundation for financials support of this work.

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